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A LITERATURE SURVEY OF THE CORROSION OF METAL ALLOYS
IN LIQUID AND GASEOUS FLUORINE

By

J. H. Cabaniss and J. G. Williamson

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ABSTRACT

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A literature survey on the corrosive nature of both liquid and gaseous fluorine is presented. This paper contains general information regarding: (1) chemical reaction of fluorine with various metallic materials; (2) conditions under which these materials can be used with fluorine; (3) results of corrosion tests that have been conducted on various materials over the temperature range of $-320^{\circ}F$ ($-196^{\circ}C$) to $1300^{\circ}F$ ($704^{\circ}C$).

Author

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MATERIALS DIVISION
PROPULSION AND VEHICLE ENGINEERING LABORATORY

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SUMMARY

Although fluorine is the most chemically active element known, many common metal alloys can be used for handling this material. This is possible because fluorine forms a fluoride film on many metals which is non-volatile, insoluble, and strongly adherent. Meticulous cleaning and passivation procedures must be followed to form this film. Many factors, such as alloying elements in the metal, the flow rate, pressure and temperature of the fluorine, and contaminants in the fluorine, affect this fluoride film, and, consequently, affect the general reaction rates of fluorine with metal alloys. Contaminants in the fluorine, such as water, hydrogen fluoride, hydrogen peroxide, oxygen, oxygen difluoride and ozone, can greatly influence the reaction of fluorine with all metals.

Under certain conditions, aluminum, low alloy steels, copper, and many other metal alloys can be used for fluorine service at normal temperatures; whereas, many more metals can be used at low temperatures. However, as the temperature of fluorine increases, fewer and fewer metal alloys are suitable. Chromium and nickel plate and low silicon steels are suitable to 400°F (204°C), low silicon and low carbon steels and iron to 600°F (316°C), copper and copper alloys to 850°F (454°C), some aluminum and magnesium alloys to 900°F (482°C), and nickel and nickel alloys to 1200°F (649°C).

INTRODUCTION

Before development of the atomic bomb, the production of fluorine was limited to laboratory quantities. Since then, extensive work has been performed to increase the information on the properties and reactions of this element. Early in the development of space vehicles, the advantages of fluorine as an oxidizer for liquid propellant engines were recognized. Interest in using fluorine, particularly for upper stages, has increased in recent years. This is a natural response since liquid fluorine, in combination with most fuels, gives higher performance values than any other oxidizer.

The lack of vital information concerning the reactions and the corrosive nature of liquid fluorine with materials of construction has had a deterrent effect on its application as an oxidizer for vehicle engines. Until recently, most work with fluorine for use with space vehicles has been concerned with engine performance; consequently, engine hardware and handling equipment were fabricated from materials known to be compatible with fluorine rather than with the more common engineering materials.

The purpose of this paper is to review and summarize the recent corrosion studies conducted on liquid and gaseous fluorine. It may also be used as a guide in selecting the proper materials for use in handling fluorine.

GENERAL CORROSIVE CHARACTERISTICS
OF LIQUID AND GASEOUS FLUORINE

General Reactions

Fluorine, under the right conditions, will react with nearly all known elements and compounds except the elemental fluorides in their highest valence state (Ref. 1 and 2). In addition to the extremely difficult problems of chemical reactivity, liquid fluorine, with a boiling point of -304°F (-187°C), imposes the same limitations on materials as other cryogenic liquids. One of the controlling factors for corrosion of materials in liquid fluorine is the degree of solubility of the fluoride film which forms on the surface of metal alloys (Ref. 3). Some metals and alloys form a tenacious, ductile, fluoride film. Some form gaseous or liquid films even at room temperature, and others form brittle, porous, spongy, and powdery films; this makes the selection of materials for

use with fluorine very difficult. Table I lists metals and elements that form gaseous or low melting fluorides (Ref. 2, 3, and 4). Metal alloys containing appreciable amounts of one or more of the elements listed in Table I would not be good structural materials for handling fluorine at room temperature, although they may perform adequately at cryogenic temperatures. The fluorides of nickel, beryllium, copper, chromium, iron, aluminum, and some magnesium alloys are fairly insoluble in liquid fluorine.

In a report by J. D. Jackson (Ref. 5), it was noted that a type of fluoride film was responsible for preventing high corrosion rates and that the purity of the fluorine gas also might affect the corrosion rate. The effect of the purity of fluorine has been found, in later work, to greatly affect the corrosion rate of various metal alloys--this will be discussed later in this paper.

Corrosive Effects of Flow and Pressure

H. W. Schmidt of Lewis Flight Propulsion Laboratory conducted a series of tests to determine the effects of flow and pressure on 2024-0, 5052-0, and 1100 aluminum alloys, 304, 316, 347, 420, and 440 stainless steels, yellow brass, and nickel (Ref. 6). The metal specimens, in selected geometric shapes, were exposed to liquid fluorine under controlled conditions of flow and pressure. None of the samples exhibited any measurable physical or chemical changes. In a special test, teflon was subjected to flowing fluorine at 50 psi, and an instantaneous chemical reaction, which completely destroyed the piece, occurred. Mr. Schmidt stated that fluid friction and impact effects, resulting from high pressure, high velocity, liquid fluorine flowing past irregularly shaped or sharp edged objects, were not likely to initiate fluorine systems failure. It was also evident that teflon should not be used in any area where it will be subjected to pressure or flow.

A Battelle Memorial Institute Report (Ref. 7) stated that high flow rates tend to remove protective films from the metals which may increase the attack rate, and if particles are loosened, difficulties could occur at valves and other restricted areas. Kleinberg and Tompkins (Ref. 8) stated that there was some doubt that loosening the protective film should appreciably increase the rate of attack in fluorine; however, this could possibly occur if the metal fluoride is continually eroded away.

TABLE I

LOW MELTING ELEMENTAL FLUORIDES

Element	Fluoride	Melting Point °F	Boiling Point °F
Nitrogen	NF_3	-358	-164
Carbon	CF_3	-299	-198
Oxygen	OF_2	----	-269
Boron	BF_3	-197	-150
Silicon	SiF_4	-141	-140
Hydrogen	HF	-117	67
Phosphorus	PF_3	-256	-150
	PF_5	-137	-121
Sulfur	SF_6	-83 Sublimates	
Arsenic	AsF_3	15	145
	AsF_5	-112	-63
Molybdenum	MoF_6	63	95
Tungsten	WF_6	36	68
Vanadium	VF_5	----	232
Niobium	NbF_5	162	428

Metal fluorides that are brittle, powdery, or porous will loosen
when subjected to pressure, flow, or shock, and the metal will then be
attacked at the same high initial rate as that of an unpassivated system.
This process would soon affect the structural integrity of the material.
This is one of the reasons that several of the workers in this field have
reported that, before installing any new systems, the materials to be
used should be tested in an environment similar to that of the proposed
operating system (Ref. 1, 4, 7, 9, 10, 11, 12, and 13).

R. B. Jackson (Ref. 10) discussed tests conducted to determine the
effects of pressure and temperature on several metals. The data from
these tests are shown in Table II. Test temperatures were 80°F (26.7°C),
400°F (204°C), 700°F (371°C), and 1000°F (538°C), and the initial pressure
was 250 psi. The report stated that the metals were not affected
uniformly, and from the data it was impossible to determine the total
effect of the pressure at the different temperatures. It was concluded
that additional tests should be conducted to determine the maximum safe
operating temperature at different pressures for all common engineering
materials.

Effects of Temperature and Temperature Cycling

Godwin and Lorenzo (Ref. 14) conducted a series of tests to determine
the ignition temperature of some common metals in fluorine (Table III).
The tests consisted of heating a wire in the presence of fluorine until
it burst into flames. It may be noted from Table III that nickel, copper,
aluminum, and iron have high ignition temperatures.

Several studies have been made to determine the effects of static
fluorine on different metals over a wide temperature range (Ref. 3, 5,
8, 10, 11, 12, 13, 15, 16, 17, and 18). The studies showed, generally, that
in an unstressed, static system the corrosion rate decreased as the
temperature decreased to -320°F (-196°C) and as the length of the test
extended beyond 24 hours. It was also noted that as the temperature was
increased the material became highly susceptible to burning or exploding.

Steindler and Vogel (Ref. 16) found that at high temperatures nickel
and copper were the best materials for fluorine, and even copper would
not be usable above 1000°F (538°C). Alumina and calcium fluoride ceramic
were tested and found to have excellent resistance to fluorine up to 1382°F
(750°C); also, they have a much lower corrosion rate than nickel or the
nickel copper alloys.

TABLE II

EFFECTS OF FLOW AND PRESSURE ON THE CORROSION RATES OF MATERIALS IN GASEOUS FLUORINE

Material	Exposure Time (Hr)	Corrosion Rate (Inches/Year)						
		* Temperature				** Temperature		
		80°F	400°F	700°F	1000°F	400°F	700°F	1000°F
Aluminum 1100	5	.0080	.0020	.0061	1.822			
	24	.0024	.0018	.0295	.1965	.0004	.1654	.1999
	120	.0002	.0000	.0750	.2867			
Aluminum 2024	5	.0079	.0010	.0020	.0293			
	24	.0005	.0018	.0013	.9063	.0013	.0314	-----
	120	.0001	.0001	.0067	.0014			
Aluminum 5154	5	.0081	.0041	.0050	.0078			
	24	.0020	.0019	.0016	.0061	.0032	.0005	-----
	120	.0002	.0004	.0005	.0012			
Magnesium M1A	5	.0000	.0010	.0074	.0727			
	24	.0024	.0017	.0024	.0157	.0017	.0010	-----
	120	.0002	.0002	.0009	.0104			
Magnesium AZ81	5	.0000	.0013	.0131	.0394			
	24	.0020	.0008	.0041	.0092	.0062	.0041	-----
	120	.0001	.0002	.0003	.0028			
Magnesium AZ91	5	-----	-----	-----	-----			
	24	.0017	.0003	.0026	.0289	.0072	.0045	-----
	120	.0002	.0001	.0011	.0011			
Monel	5	.0024	.0005	.0019	.0298			
	24	.0005	.0005	.0017	.0113	.0007	.0024	.0213
	120	.0002	.0001	.0012	.0072			
Nickel A	5	.0010	.0033	.0017	.0245			
	24	.0009	.0005	.0012	.0161	.0003	.0005	.0445
	120	.0000	.0001	.0004	.0138			
Stainless Steel 304	5	.0017	.0061	1.565	-----			
304L	24	.0006	.0075	6.018	-----	-----	-----	-----
304L	120	.0000	.0254	-----	-----			

*Corrosion rate in a stream of gaseous fluorine 100 ml/min.

**Corrosion rates in gaseous fluorine under an initial pressure of 250 pounds gauge.

TABLE III   7

IGNITION TEMPERATURES OF SELECTED METALS IN FLUORINE

Metal	Number of Tests	Ignition Temp. °F	Average Ignition Temp. °F	% Maximum Variation from Average
Aluminum	4	*	1382	----
Copper	5	1337 1193 1238 1238 1377	1277	8.0
Iron	4	1251 1233 1233 1249	1242	0.8
Molybdenum	5	394 381 354 408 354	378	8.3
Monel	4	818 793 698 710	755	12
Nickel	6	2134 2005 2226 2183 2208 1983	2091	6
302 Stainless Steel	4	1380 1465 1132 1058	1259	13
Tungsten	4	446 565 473 500	496	18

*An average of 4 tests gave an ignition temperature greater than the melting point of Aluminum (1220°F).

M. H. Brown (Ref. 12) tested the resistance of several metals and alloys to hydrogen fluoride and fluorine. The results of these short duration tests showed that nickel is an excellent high temperature material. The author noted the interesting effects of very small amounts of silicon in alloys of iron; even 0.2% silicon greatly increased the corrosion rate on iron alloys at temperatures up to 700°F (371°C). Above 700°F, iron alloys have a tendency to combine rapidly with fluorine.

Gundzik and Feiler studied the effects of temperature cycling on six different alloys (Table IV, Ref. 19). These metals were exposed to liquid fluorine for 13 hours a day, 5 days a week. (The metals were allowed to return to room temperature during the remaining 11 hours of the day and on week-ends.) Duration of the first test period was 1.5 months; the second test lasted 3.5 months. At the end of these tests, no visible or measurable difference between these specimens and those exposed only to gaseous fluorine was noted.

Effects of Contaminants in Fluorine

Water or water vapor in a fluorine system will cause considerable damage. The water reacts with fluorine to form hydrogen fluoride, hydrofluoric acid, hydrogen peroxide, oxygen difluoride, ozone, and oxygen (Ref. 3). In a liquid fluorine system, hydrogen fluoride and hydrogen peroxide will be solid; however, oxygen, oxygen difluoride, and ozone are all soluble in fluorine throughout its liquid range. These contaminants will increase the rate of corrosion on all metals. Also, the reaction of water vapors with fluorine can often be inhibited until enough water vapor accumulates to cause an explosion (Ref. 8 and 13). Therefore, even though it may be extremely difficult in large systems, the removal or exclusion of water from a fluorine system is highly desirable. H. R. Leech (Ref. 20) stated that if water is excluded from a system mild steel can be used for fluorine equipment in temperatures up to 600°F (316°C) and that most of the problems in handling fluorine or hydrogen fluorine are caused by contamination and not by the reaction of fluorine with the metals.

Personnel at Air Products (Ref. 8, 11, 15, and 21) isolated and tested several contaminants to determine their effects on various metals. Corrosive effects of these contaminants were noticeable in concentrations of .2%. Oxygen difluoride is soluble in liquid fluorine in all concentrations and is extremely difficult to remove (Ref. 8). Hydrogen fluoride forms

TABLE IV

TEMPERATURE CYCLING EFFECTS ON METALS*

Metals	Weight Change Mg./Sq. In. (Internal Area)		Average Corrosion Inches Penetration/Year	
	A	B	A	B
3003-0 Aluminum	0.18	1.33	3.12×10^{-5}	8.88×10^{-5}
5052-0 Aluminum	0.68	1.48	12×10^{-5}	10.2×10^{-5}
347 Stainless Steel	0.09	0.49	1.2×10^{-5}	2.3×10^{-5}
321 Stainless Steel	0.26	0.43	3.14×10^{-5}	2.04×10^{-5}
Nickel (A)	0.06	0.63	0.5×10^{-5}	2.04×10^{-5}
Brass (Low Lead)	0.64	1.99	6.24×10^{-5}	7.56×10^{-5}

*Basic cycle: 13 hours in liquid fluorine, 5 days a week (11 hours a day and on week ends, allowed to return to room temperature).

A - Cycled in fluorine a total of 1055 hours.

B - Cycled in fluorine a total of 2730 hours.

hydrofluoric acid which causes corrosion of aluminum, magnesium, and steel. Only nickel, copper, and their alloys are usable in systems that are contaminated with hydrogen fluoride. In analyzing several grades of commercial fluorine gas, it was found that contamination was as high as 25% of the total volume of the fluorine (Ref. 22). Of this 25%, only the oxygen difluoride cannot be removed by filters and cooling (Ref. 10). It has been noted that proper care in manufacturing, transfer, and storage would alleviate most of the contaminants in the fluorine (Ref. 8).

Cleaning of Fluorine Systems

In fluorine systems, the preparation of the materials before the introduction of fluorine is as important as the proper selection and use of materials (Ref. 23). Absolute cleanliness is a prime requirement for all systems which handle fluorine. Minute amounts of a contaminant can cause overheating, fires, and explosions in the system which will continue until all the contaminant is fluorinated or until all the fluorine is depleted (Ref. 3). In many instances, the heat generated is sufficient to trigger a reaction (Ref. 17) with materials which are normally stable. At most installations using fluorine, some loss of equipment by fire or explosion has been traced to contaminants in the system (Ref. 20, 24, 25, and 26). These hazards may be overcome by immaculate cleaning and passivation of components in a system. All of the installations using fluorine have special procedures to follow for cleaning and passivating a fluorine system (Ref. 1, 3, 5, 9, 10, 16, 17, 20, 22, 23, 24, 25, 26). Although procedures may differ somewhat, each follows the same basic steps as follows:

    a. Degrease and remove dirt and light contaminants.

    b. Dry and inspect for cleanliness.

    c. Reclean all parts necessary. (Usually, this step is needed on brazed, welded, and soldered pieces and includes such methods for cleaning as sand blasting, wire brushing, and other mechanical methods or the use of heavy duty alkaline or acid scale removers.)

    d. Rinse, dry, and re-inspect for cleanliness.

    e. Insure that all surfaces are clean, by using one of the nitric-hydrofluoric acid solutions as a final cleaner.

f. Rinse, flush with solvent, and dry. (For drying, use warm, clean, dry, oil free nitrogen or helium '.

g. Final passivation with dilute fluorine. [This final step is usually accomplished by diluting fluorine with nitrogen or helium. The step normally requires several hours - because the fluorine is started out as a 10% mixture, and the concentration is gradually increased until the system has 100% fluorine at a temperature and pressure slightly higher than that of the normally operating system (Ref. 4, 18, 24, and 25)].

Under the proper conditions, this procedure will remove all traces of contaminants and start the formation of the relatively inert fluoride films (Ref. 2). By starting with a dilute gas, there is considerably less chance of the contaminants catching fire.

CORROSIVE EFFECTS OF FLUORINE ON VARIOUS METALS

Aluminum and Aluminum Alloys

Fluorine reacts with aluminum to form aluminum fluoride, which is very stable and affords the aluminum surface good protection. Although aluminum and its alloys form a tenacious oxide film which cannot be removed by reduction, fluorine will react with this oxide coating first and then with the unreacted metal underneath to form the aluminum fluoride film. As is true with nickel, copper, and iron, adding alloying elements to aluminum lowers the protection against further attack. For example, the one to two percent silicon aluminum alloys cannot be completely passivated until all of the silicon is depleted, and depletion o   e silicon will greatly weaken the alloys. This could present a problem at welds also because several of the welding alloys contain silicon. Hydrogen fluoride forms a complex with aluminum fluoride which destroys the protective qualities of the fluoride film and allows the fluorine to attack the aluminum at a rate approaching that of unpassivated aluminum. Moisture does not directly affect the aluminum fluoride film, although one of the reaction products of moisture and fluorine, hydrofluoric acid, will cause adverse effects. Aluminum may be used for cryogenic tanks and in areas where hydrogen fluoride contamination in fluorine is very low. The corrosion rates of some common aluminum alloys in fluorine are given in Table V.

TABLE V

CORROSION OF ALUMINUM IN FLUORINE

Metal Aluminum	Reference	Test Duration (hrs)	Corrosion Rates (Inches/Year) According to Temperature (°F)				
			-320 to -310	50 to 250	250 to 450	450 to 750	750 to 1000
1100-H14	10	5	876 x 10⁻⁴	0.0805	0.0020	0.0061	1.822
	10	24	--------	0.0024	0.0031	0.0295	0.1965
	10	24	--------	------	0.0004	------	------
	10	120	--------	0.0002	.0000	0.075	0.2875
	18	5	--------	------	------	0.0000	0.156
	5	5	90 x 10⁻⁴	------	------	------	------
	11	*	0.6 x 10⁻⁴	------	------	------	------
	8	*	0.2 x 10⁻⁴	------	------	------	------
2017	11	*	1.3 x 10⁻⁴	------	------	------	------
2024-T3	10	5	1665 x 10⁻⁴	.0079	.0010	.0020	.0294
	10	24	--------	.0005	.0008	.0013	.0063
	10	24	--------	------	.0028	------	------
	10	120	--------	.0001	.0001	.0066	.0014
	5	5	1500 x 10⁻⁴	------	------	------	------
3003-H14	10	5	2103 x 10⁻⁴	.0009	.0005	.0010	.0215
	10	120	31 x 10⁻⁴	------	------	------	------
	5	5	30 x 10⁻⁴	------	------	------	------
5052	11	*	2 x 10⁻⁴	------	------	------	------
5154-H34	10	5	1878 x 10⁻⁴	.0081	.0040	.0050	.0074
	10	24	--------	.0005	.0016	.0016	.0060
	10	24	--------	------	.0021	------	------
	10	120	--------	.0002	.0004	------	------
5154-0	10	120	--------	------	------	.0004	.0013
	5	5	900 x 10⁻⁴	------	------	------	------
6061	11	*	1 x 10⁻⁴	------	------	------	------
	8	*	2 x 10⁻⁴	------	------	------	------
7079	11	*	1 x 10⁻⁴	------	------	------	------
Sheet	3	5	--------	------	------	------	.48-.72

*Test Duration not specified

Iron and Low Alloy Steels

The reaction of iron with fluorine produces a weakly adhering mixture of ferrous and ferric fluorides which are easily damaged (Ref. 3, 8, 12, 14, and 17). This problem of flaking and the highly damaging effects of hydrogen fluoride limit the use of iron in fluorine systems. The iron fluoride film was compared with the nickel fluoride film and found to be less than one one-hundredth as protective as nickel fluoride. The iron fluoride film is also very unstable in the presence of moisture, which further limits the area of use. The addition of up to five per cent nickel or chromium produces very little change in the resistance of iron to fluorine attack, and some of the iron alloys may be as much as 50 times more susceptible to corrosion than pure iron under the same conditions. The corrosion rates of iron and steel alloys in fluorine are given in Table VI. The mild steels may be used for storage and handling equipment in temperatures to approximately 400°F (204°C); Armco iron has a little more resistance and could possibly be of use at temperatures to approximately 600°F (316°C) (Ref. 3). Many of the alloying agents (carbon, silicon, phosphorus, arsenic, sulfur, and boron) produce volatile fluorides which could contribute to pitting or intergranular corrosion.

Stainless Steel

The 18-8 series stainless steels have little or no advantage over mild steel in fluorine handling except for cryogenic properties. In fact, the presence of silicon, molybdenum, niobium, and carbon (all of which form volatile fluorides) contributes to pitting attack of the stainless steels (Ref. 17). These alloys have better resistance in the annealed condition than in the cold worked condition, and the 347 alloy is more resistant than the 302 alloy. The 300 series stainless steels should not be used at temperatures above 300°F (149°C) since the chromium fluorides are volatile above this temperature.

Nickel Based Alloys

The reaction of nickel and Monel with fluorine and fluorinating agents has been studied under a wider variety of conditions than any other metal. The variables studied include temperature (Ref. 5, 17, 25, 26, and 19), pressure (Ref. 6), exposure time (Ref. 10), fluorine concentration in the gas phase, dynamic conditions versus static conditions, film thickness, surface conditions, and configuration

TABLE VI

CORROSION OF IRON AND STEEL IN FLUORINE

Metal Steel	Reference	Corrosion Rates (Inches/Year) According to Temperature (°F)									
		-320 to -310	50 to 100	100 to 200	250 to 400	400 to 500	500 to 600	600 to 700	700 to 800	800 to 900	900 to 1000
Low Carbon Steel	10*	267×10^{-4}	.0047		.0047			.3986			Consumed
Low Silicon Iron	3				.0037						
High Silicon Iron	3				.0067						
Sheet Iron .007% Si	18					.192	.048	.0024	.144		88.8
SAE 1010	27			.0001							
SAE 1015	18						9.96				
SAE 1020	12				.4524	5.76	11.04	1.74	3.16	18.24	178.8
SAE 1030	18				.456	.576	7.82	1.764	6.48	18.24	
SAE 1030	18				.108	.180	232				
SAE 1030	18				Nil	6.48					
Music Wire	18			.0007			4.8				132.0
Armco Iron	3							.096	.288	3.6	139.2
Armco Iron	18					.024	.108				
Armco Iron	12				.0024	.0024		.0984	2.832	3.6	139.2
Mild Steel	5	2.40×10^{-4}									
Mild Steel	12				.0072	.1932	.0528		.1368	3.5	88.8
27% Carbon Steel	12					.0942			1.836	6.48	237.6
15-7 (MO) PH	11	2×10^{-4}									
15-7 (MO) PH	8	$.1 \times 10^{-4}$									
AM 350	11	4×10^{-4}						1.588			
304 Stainless	10*	1376×10^{-4}	.0017			.0061					
304 Stainless	5	200×10^{-4}									
304 Stainless	11	$.2 \times 10^{-4}$									
304 Stainless	8	$.25 \times 10^{-4}$									
304 Stainless	10**	56×10^{-4}									
309 (Cb) Stainless	18						.9	5.544	7.98		
310 Stainless	18	4×10^{-4}					.408	4.248	6.732		
316 Stainless	11										
347 Stainless	10*	1577×10^{-4}	.0027			.0038			4.248		
347 Stainless	5	1180×10^{-4}				1.72	2.556	6.2	9.54		
347 Stainless	18										
347 Stainless	11	$.4 \times 10^{-4}$									
410 Stainless	8	$.6 \times 10^{-4}$									
420 Stainless	11	3×10^{-4}									
430 Stainless	11				.0084		3.060	.936	.936		

#Five hour test
##One hundred and twenty hour test
(Other items not specified)

(Ref. 3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, and 18). Hydrogen fluoride reacts slowly with nickel at moderate temperatures, and the fluoride film does not completely protect nickel against this attack. Sulfur in the fluorine will also increase fluorine's attack on nickel. It has been noted that nickel "A", "D", and "L" and Monel may be used for fluorine equipment in the temperature range of -320°F (-196°C) to +1200°F (649°C) although Monel, "K" Monel, and "S" Monel may be preferred for any service where hydrogen fluoride or other contaminants are present (Ref. 3, 7, 8, 10, and 17). Welding does not reduce the corrosion resistance of nickel or Monel if fluxes are not used or are completely removed. Inconel, Illium, Illium "R", and Duranickel offer less resistance than either nickel or Monel, and the maximum usable temperature for these alloys is about 750°F (398.9°C). Other high nickel alloys (Nichrome, Mumetal, etc.) have been tested with less favorable results (Ref. 2, 6, 7, 11, and 17). The corrosion rates of nickel and nickel alloys in fluorine are given in Table VII.

Copper Alloys

Copper forms two fluorides, cuprous and cupric, which, when allowed to stand or when exposed to extended fluorine service, become all cupric fluoride. Copper and nickel suffered approximately the same rate of fluorine attack, and the total fluoride film thickness on copper, after a given exposure time, was approximately two times that of nickel in the temperature ranges studied (Ref. 17). Copper has a high resistance to fluorine attack to approximately 930°F (498.8°C) (Ref. 3). Higher rates of attack on copper can be expected when the fluorine is contaminated with oxygen (Ref. 2). The copper alloys, red brass, yellow brass, and bronze are usable to approximately 500°F (265.6°C). Although little empirical data are available on these copper alloys, it is known that fluorine selectively attacks these alloys. Fluorine reacts with zinc and tin in brasses, causing a type of intergranular corrosion; the lead-copper alloys are rapidly penetrated due to the poor solubility of lead in copper and the nonadhesive characteristic of lead fluoride. Except for grade A phosphor bronze, the room-temperature fluorine corrosion rate of the single-phase copper alloys is from two to ten times that of pure copper; the two-phase alloys may have a corrosion rate 100 times greater (Ref. 17). Generally, the use of alloys containing lead, phosphorus, and silicon in copper, beyond the solubility limits for these elements, should be avoided if the highest resistance to fluorine attack is desired. The cupric fluoride film is very protective against hydrogen fluoride, but is very unstable in moisture, and very small amounts of moisture

TABLE VII

CORROSION OF NICKEL AND NICKEL ALLOYS IN FLUORINE

Nickel Alloy	Reference	-320 to -310	\Corrosion Rates (Inches/Year) According to Temperature (°F)										
			50 to 250	250 to 400	400 to 550	550 to 700	700 to 800	800 to 900	900 to 1000	1000 to 1100	1100 to 1200	1200 to 1300	1300 to 1400
A	10*	241×10^{-4}	.001	.0033	----	----	.0017	----	----	.0246	----	----	----
A	10**	----	.0009	Nil	.0010	----	.0012	----	.0156	.0138	----	----	----
A	10⧸	----	Nil	.0001	----	.0004	----	----	----	----	----	----	----
A	5	25×10^{-4}	.0024	----	.0032	----	----	----	----	----	----	----	----
L	10*	359×10^{-4}	----	----	----	----	.0014	----	----	.0201	----	----	----
L	5	25×10^{-4}	----	----	----	----	----	----	----	----	----	----	----
D	2	----	----	----	----	----	----	----	----	----	.002	----	----
99.4%	18	----	----	----	----	----	.0084	.0228	.0612	----	.348	.192	.408
99.4%	11	$.2 \times 10^{-4}$	----	----	----	----	----	----	----	----	----	----	----
99.4%	8	7.3×10^{-6}	----	----	----	----	----	----	----	.0002	----	.314	.816
99.4%	16	----	----	----	----	----	----	----	----	----	.0003	----	----
Low Carbon	2	----	----	----	----	----	----	----	----	----	.0008	----	----
Duranickel	2	----	----	----	----	----	----	----	----	----	----	----	----
Illium	10*	900×10^{-4}	.0020	.0062	----	.0127	----	----	4.04	----	----	----	----
Illium R	5	100×10^{-4}	----	.0010	----	.0019	----	----	----	----	----	----	----
Monel	10*	1603×10^{-4}	.0025	.0010	----	----	.0018	----	----	.0298	----	----	----
Monel	10**	146×10^{-4}	.0005	----	.0010	----	----	----	----	.0113	----	----	----
Monel	10⧸	52×10^{-4}	.0002	.0002	----	.0012	----	----	----	----	----	----	----
Monel	18	----	----	----	----	----	.006	.018	.024	----	.0072	.96	1.8
Monel	5	20×10^{-4}	----	----	----	----	----	----	----	----	----	----	----
Monel	19	$.5 \times 10^{-4}$	----	----	----	----	----	----	----	----	----	----	----
Monel	8	84×10^{-4}	----	----	----	----	----	----	----	----	----	----	----
Monel	16	----	----	----	----	----	----	----	----	----	----	Nil	3.5
Monel Cast	10*	1180×10^{-4}	.0020	.0010	----	----	.0039	----	.0429	----	----	----	----
Monel Cast	5	125×10^{-4}	.0017	.0012	----	.0775	----	----	----	----	----	----	----
Inconel	10	267×10^{-4}	----	----	----	----	.456	----	3.451	----	----	----	----
Inconel	18	----	----	----	----	----	----	1.152	.744	----	2.04	1.52	6.12
Inconel	5	250×10^{-4}	----	----	----	----	----	----	----	----	----	----	----
Inconel	16	----	----	----	----	----	----	----	----	4.8	----	6.0	33.5

*Five hour test
**Twenty-four hour test
⧸Five day test
(Other tests duration not specified)

will destroy the passive fluoride film on all copper alloys (Ref. 10).
The corrosion rates of copper and copper alloys in fluorine are given
in Table VIII.

Magnesium

Magnesium, like aluminum, is always coated with an oxide film
which cannot be removed by reduction, even with hydrogen. The
passivation of magnesium follows the same steps as for aluminum:
the conversion of the oxide film to a fluoride and the fluorination of
the metal underneath. Hydrogen fluoride mixed into the fluorine will
prevent the formation of a completely protective film, which, then,
allows the metal to be continuously attacked until completely destroyed.
Magnesium may be used in areas where moisture and hydrogen fluoride
will not be present or for short life service. The corrosion rates of
magnesium alloys in fluorine are given in Table IX.

Titanium

Titanium does not form a very protective high-temperature fluoride
film, and fluorine will rapidly attack the metal at temperatures above
$300^{\circ}F$ ($149^{\circ}C$). There have also been cases reported where titanium
was ignited at $-113^{\circ}F$ ($-81^{\circ}C$) although the authors noted that, generally,
a catalysis was necessary and the reaction was smothered by the fluoride
film (Ref. 3 and 15). Because of the probability of impact sensitivity,
titanium should not be considered for use in fluorine systems.

Miscellaneous Metal Alloys

Silver solders are recommended for most of the joining where
welding is impractical or impossible (Ref. 3 and 9). Silver is not very
resistant to fluorine, but the addition of copper greatly improves its
resistance to attack. The addition of zinc and cadmium lowers the
resistance of silver solder to corrosion but increases workability of
the solder. Thus, the lower corrosion resistant solder is sometimes
preferred to the more resistant hard-to-work solders (Ref. 3). Soft
solders should be avoided because of the high tin and lead content.

Chromium forms four fluorides: (1) divalent, (2) trivalent,
(3) tetravalent, (4) pentavalent. (The last two are volatile.) When chromium
is reacted with fluorine below $300^{\circ}F$ ($149^{\circ}C$), it forms a very protective

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TABLE VIII

CORROSION OF COPPER AND COPPER ALLOYS IN FLUORINE

Metal	Reference	Corrosion Rates (Inches/Year) According to Temperature (°F)						
		-320 to -310	50 to 250	250 to 450	650 to 850	850 to 1000	1000 to 1250	1250 to 1400
Copper								
ETP	10*	1577×10^{-4}	.0033	.0072	.0308	.2322	-----	-----
Deoxidized	18	-----------	-----	-----	1.92	1.44	11.88	34.8
	5	1500×10^{-4}	-----	-----	-----	-----	-----	-----
Electrolytic Grade	11	4×10^{-4}	-----	-----	-----	-----	-----	-----
	8	$.03 \times 10^{-4}$	-----	-----	-----	-----	-----	-----
Sheet	2	-----------	-----	-----	-----	2.4	-----	36.0
	22	-----------	-----	-----	-----	-----	.54	1.10
Brass								
American #243	10*	556×10^{-4}	.0175	.0202	.3811	3.85	-----	-----
	5	600×10^{-4}	-----	-----	-----	-----	-----	-----
Red Brass	10*	1577×10^{-4}	.0025	.0056	.0709	.3940	-----	-----
	5	1600×10^{-4}	-----	-----	-----	-----	-----	-----
Yellow Brass	11	5×10^{-4}	-----	-----	-----	-----	-----	-----
Cartridge Brass	11	2×10^{-4}	-----	-----	-----	-----	-----	-----
Casting Brass	11	15×10^{-4}	-----	-----	-----	-----	-----	-----
Everdur 1010	11	8×10^{-4}	-----	-----	-----	-----	-----	-----
90% Cupro-Nickel	11	2×10^{-4}	-----	-----	-----	-----	-----	-----
70% Cupro-Nickel	11	6×10^{-4}	-----	-----	-----	-----	-----	-----

* 5 hour test
(other tests duration not specified)

TABLE IX

CORROSION OF MAGNESIUM AND MAGNESIUM ALLOYS IN FLUORINE

Metal	Refer- ence	Test Duration Hrs	Corrosion Rates (Inches/Year) According to Temperature (°F)								
			-320 to -310	50 to 200	200 to 400	400 to 500	500 to 600	600 to 700	700 to 900	900 to 1000	1000 to 1100
Magnesium M1A	10	5	1314×10^{-4}	Nil	-----	.0019	-----	-----	.0079	.0394	-----
M1A	10	24	-----	.0041	.0017	.0017	-----	.0024	-----	-----	.0158
M1A	10	120	-----	.0003	.0002	-----	-----	.0008	-----	-----	.0106
M1A	5	*	220×10^{-4}	-----	-----	-----	-----	-----	-----	-----	-----
Dow Metal G	18	*	-----	Nil	Nil	Nil	Nil	-----	-----	-----	-----
AZ81C-T6	10	5	2844×10^{-4}	Nil	-----	.0013	-----	-----	.0131	-----	.0394
AZ81C-T6	10	5	8466×10^{-4}	-----	-----	-----	-----	-----	-----	-----	-----
AZ81C-T6	10	24	-----	.0020	.0011	.0004	-----	-----	.0039	.0092	.0216
AZ81C-T6	10	120	255×10^{-4}	.0002	.0002	-----	-----	.0003	-----	-----	.0033
AZ81C-T6	5	*	429×10^{-4}	-----	-----	-----	-----	-----	-----	-----	-----
HK31A-H24	10	5	1226×10^{-4}	.0055	.0066	-----	-----	.0067	-----	.0201	-----
HK31A-H24	10	5	450×10^{-4}	-----	-----	-----	-----	-----	-----	-----	-----
HK31A-H24	5	*	-----	-----	-----	-----	-----	-----	-----	-----	-----
AZ91C-T6	10	24	-----	.0017	-----	.0003	-----	.0027	-----	.0289	.2313
AZ91C-T6	10	120	-----	.02	-----	.0002	-----	.0011	-----	-----	.0015

*Time not specified

divalent fluoride that is similar to the film on nickel plate. Above
300°F, the divalent fluoride is converted to the tetravalent volatile
fluoride and loses its protective ability. Chromium may be used below
300°F with no problems other than those associated with nickel plate
(Ref. 17).

Beryllium forms a fluoride which is as protective below 600°F
(316°C) as nickel and at 750°F (399°C) only one-half as protective
(Ref. 16). Further investigations of beryllium are necessary to determine
if it could be used for certain special operations instead of aluminum
or steel.

Tantalum should not be used at temperatures above 100°F (38°C)
because it ignites at about 150°F (66°C). Because of the low ignition
point of its fluoride, not much research data are available on tantalum.

Lead forms a brittle fluoride which does not protect the parent
metal, and hydrogen fluoride rapidly attacks it at a fairly low temperature
(Ref. 17).

Tin reacts quite similararly to lead, although it has had some use as
soft gaskets in cryogenic service. Tin is also rapidly attacked by
hydrogen fluoride at all temperatures.

Rhodium, palladium, and platinum can be used in contact with
fluorine at room temperature (72°F, 22.2°C) essentially without attack.
However, because these materials form volatile fluorides at relatively
low temperatures, extreme caution must be exercised in using them in
the presence of fluorine at temperatures above 100°F (37.8°C) (Ref. 17).
These metals are used in some equipment because they are inert when
under attack by hydrogen fluoride.

Some metals show little tendency to be passivated against attack
by fluorine, even when fluorine is the passivating agent (Ref. 9 and 16).
Among such metals are alkali earth metals, niobium, columbium,
molybdenum, tungsten, uranium, lithium, sodium, potassium, rubidium,
cadmium, bismuth, silver, and gold.

CONCLUSIONS

Although fluorine is the most reactive chemical known, it can be handled with many common engineering metal alloys with only limited corrosion, particularly at the low temperature of liquid fluorine. Nickel and its alloys may be used with fluorine gases to 1200°F (649°C), some aluminum and magnesium alloys to 900°F (482°C), copper and copper alloys to 850°F (454°C), and chromium plate, nickel plate, and low silicon steel to 400°F (204°C). The corrosion resistance of a metal to fluorine is dependent on the properties of the protective fluoride film that forms on the surface. These properties are affected by temperature, flow rate, and pressure. It is of the utmost importance that all metal components to be used with fluorine be properly cleaned and passivated to insure the formation of a sound fluorine film.

In recent years it has been learned that impurities in fluorine, such as water, hydrogen fluoride, hydrofluoric acid, hydrogen peroxide, oxygen difluoride, and oxygen, will greatly increase the corrosiveness of fluorine. Many of the contradictions found in literature regarding corrosiveness of various alloys in fluorine probably may be explained by variations in the amount of contaminants in the fluorine that was used in the studies.

Although this study has shown that corrosion may be sufficiently controlled to allow the use of fluorine under a variety of conditions, it must be emphasized that fluorine is a very corrosive material, as compared to other oxidizers. Many corrosion problems could occur in a system as complicated as a space vehicle propulsion system, and the cleaning and operational procedures would be much more complicated than is normally required for systems using more conventional fuels. Many other problems, most of which are probably more serious than the corrosion problem, also exist in the use of fluorine. These problems include toxicity, reactions with non-metallic materials, and handling, and will be discussed in a later report.

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A LITERATURE SURVEY OF THE CORROSION OF METAL ALLOYS IN LIQUID AND GASEOUS FLUORINE

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The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

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